



Effect of trace species in water on the reaction of Al with water

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HIGHLIGHTS

- Water type and quality have a significant impact on Al–water reaction.
- Trace organic acid and F[−] ions in water retard the Al–water reaction.
- Other cations and inorganic anions have a negligible impact on Al–water reaction.
- The organic acid and F[−] ions form complexes with aluminol groups on Al surfaces.

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ABSTRACT

The Al–water reaction has attracted considerable attention in the past few years, because it is an economically viable way to supply hydrogen for portable and kW-grade fuel cells. The water type is found to have a significant impact on Al–water reaction. In this work, the effect of trace species in water on Al–water reaction is investigated systematically. It is found that the trace organic acids originated from the decay of botanies and animals in nature and trace F[−] ions, rather than other cations and anions, play a key role in the reaction dynamics of Al with water. The mechanism analyses reveal that the organic acids and F[−] ions form complexes with aluminol groups on Al particle surfaces to impede the hydration process of Al surface oxide film and retard the reaction of Al with water. The present results imply that a suitable water should be chosen for the Al–water reaction to generate hydrogen. At the same time, the organic acids and trace F[−] ions could be used as the agents to prevent undesirable Al–water reaction.

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1. Introduction

Metal Al has a good oxidation resistance due to a dense passive oxide film formed on its surface when it exposes to oxidation environment. However, when the Al particle sizes are down to sub-micrometer and nanometer, Al powder could completely react with water within a few hours [1], because the hydration process of the passive oxide film on small Al particles favors the formation and breakage of H₂ bubbles at Al:Al₂O₃ interface [2,3]. Recently, metal Al is viewed as a promising hydrogen-generation material for portable and kW-grade fuel cells, because it is relatively cheap and abundant in the earth's crust [4–6]. Meanwhile, 1 kg Al reacts with water to generate as high as 0.11 kg H₂.

In addition to the direct reaction of Al with water, different methods were used to activate Al in order to promote the hydrogen-generation rate and efficiency, e.g. Al reacts in an alkaline solution [6–9], alloying Al by doping Ga, In, Bi, Sn, etc. [10–18],

mechanically milling metal Al with special oxide [19–24], and Al surface modification [25–27], etc. In the meantime, many researchers found that water type and quality have a significant impact on the Al–water reaction [8,12,28–30]. For example, Rosenband and Gany [12] found that the Al–water reaction in tap and sea water is slower than that in deionized water. Wang et al. [28] found that Al–water reaction rate in deionized water is obviously higher than that in tap water, and their analyses indicated that deionized water exhibited higher solubility of Al₂O₃ than that of tap water, which is believed to be the possible cause for the significant enhancement of the corrosion of pristine metal Al in deionized water.

In fact, the main difference between different types of water is trace species in them, therefore it is the key to differentiate the effect of these trace species on the Al–water reaction dynamics in order to clarify the mechanisms behind. In this work, the trace species in deionized water, distilled water, tap water and sea water were analyzed, the effect of each species on the reaction dynamics of Al with water was investigated separately. Meanwhile, the possible mechanisms responsible for the reaction dynamics are discussed in detail.

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2. Experimental procedure

A nanometer Al powder with an average size of 98.38 nm (Shanghai St-nano Science & Technology Co., China) was used in the present model experiment. Four typical water, i.e. deionized water ($\text{pH} \approx 6.5$, resistivity $> 15 \text{ M}\Omega \text{ cm}$), distilled water ($\text{pH} \approx 6.5$, resistivity $\approx 0.3 \text{ M}\Omega \text{ cm}$), tap water ($\text{pH} \approx 7.5$, resistivity $\approx 4 \text{ k}\Omega \text{ cm}$), and sea water (China east sea, $\text{pH} \approx 7.6$, resistivity $< 50 \text{ }\Omega \text{ cm}$) were adopted in the experiment. In order to study the effect of trace species on the Al–water reaction dynamics, the following chemical agents were used: citric acid ($\text{C}_6\text{H}_8\text{O}_7$), tartaric acid ($\text{C}_4\text{H}_4\text{O}_6$), oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$), NaCl , Na_2SO_4 , NaNO_3 , NaF , CaCl_2 , MgCl_2 , KCl , ZnCl_2 , SrCl_2 , NaOH and HCl (Analytical reagent grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). In the comparative experiment, the water with different trace species was obtained by adding the above organic acids or inorganic salts in deionized water, because the detected concentration of trace metal cations and inorganic anions in deionized water is negligible ($< 0.01 \text{ ppm}$).

As the reaction of Al with water produces only one kind of gas, i.e. H_2 [26], and the amount of generated H_2 was used to characterize the reaction progress of Al with water. The Al–water reaction experiment was carried out in a closed glass reactor with a volume of $\approx 1300 \text{ ml}$, which was airtight and could keep a constant gas pressure of $< 3 \text{ bar}$ for more than 1 week. The detailed set-up of present equipment can be found in a previous work [1]. 0.5 g of pure Al powder was used in each test, which was suspended in 250 ml of water. A magnetic agitation bar with a speed of $\sim 500 \text{ rpm}$ was used to stir the mixture of water and Al powder. At the beginning, the reactor was filled by the ambient air and the initial gas pressure in the reactor is 1 bar. The hydrogen evolution could be determined by the gas pressure in the reactor. The measurement uncertainty of the system is $< 0.5\%$.

According to the ideal-gas equation, hydrogen yield α can be written

$$\alpha = \frac{(P - P_{\text{initial}})(V_{\text{reactor}} - V_{\text{H}_2\text{O}} - V_{\text{Al}})}{n_0RT}, \quad (1)$$

where P is the total gas pressure in the reactor; P_{initial} is the initial pressure in the reactor, which was measured before the hydrogen generation test; V_{reactor} , $V_{\text{H}_2\text{O}}$ and V_{Al} are the volumes of the reactor, water and Al powder, respectively; n_0 is the theoretical hydrogen moles by reacting all of metal Al; R is the gas constant and T is the reaction temperature. Moreover, at least two same tests were carried out to check the reproducibility of each hydrogen generation curve.

A pH meter (Model No. SX-620, Shanghai Sanxin Instrument Co., Shanghai, China) was used to measure the pH value of different aqueous solutions. An electric conductivity meter (Model No. DDS-11A, Shanghai Leici Instrument Co., Shanghai, China) was used to measure the conductivity of different water. X-ray diffractometry (XRD, Model No. D/max-2200, Rigaku Co., Japan) was used to analyze the phases in pure Al powder and those after reaction with water. Scanning electron microscopy (SEM, Model No. JSM-6700F, JEOL Co., Japan) was used to observe the morphology of as-received Al powder. An ion chromatograph (IC, Model No. MIC-II, Metrohm Co., Switzerland) was used to measure the anions in water. An inductively coupled plasma atomic emission spectrometer (ICP-AES, Model No. iCAP 6300, Thermo Fisher Co., USA) was used to measure the cations in water. A total organic carbon analyzer (TOC, Model No. Multi N/C 2100, Analytik Co., Germany) was used to measure the concentration of organic substance in water.

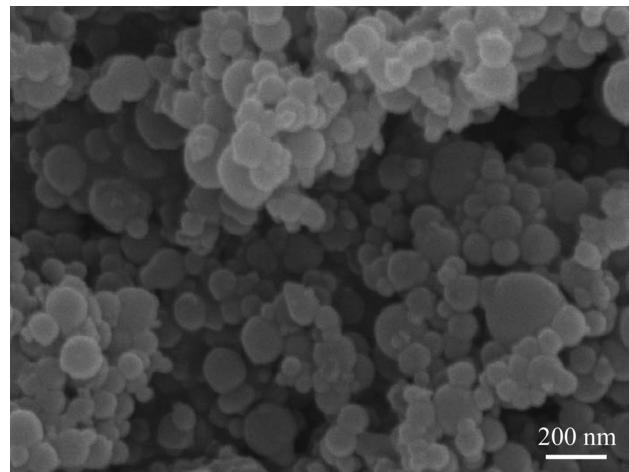


Fig. 1. SEM micrograph of as-received pure Al powder with an average size of 98.38 nm.

3. Results and discussion

3.1. Al–water reaction tests

Fig. 1 shows the morphology of as-received nanometer Al powder used in this work, basically Al particles are spherical. The Al–water reaction using different types of water at 40 °C without stirring is shown in Fig. 2 (the temperature of 40 °C makes the Al–water reaction time suitable for the present model experiment). It can be seen that nanometer Al powder could react with water at a mild temperature, and there is an induction time for the beginning of the reaction. However, the water type has a significant impact on the Al–water reaction dynamics. The reaction of Al with deionized and distilled water is clearly faster than that with tap and sea water. The reaction induction time of Al with deionized and distilled water is shorter than that with tap and sea water. The reaction of Al with sea water is the slowest among four types of water. The reaction dynamics difference between deionized water and distilled water is small. Table 1 gives the maximum hydrogen generation rate (MHGR) and induction time of Al powder in different types of water. The induction time of Al with deionized water is $\sim 0.6 \text{ h}$, and $> 80\%$ of Al was consumed and generated H_2 within 2 h, indicating that nanometer Al powder is a promising hydrogen-generation

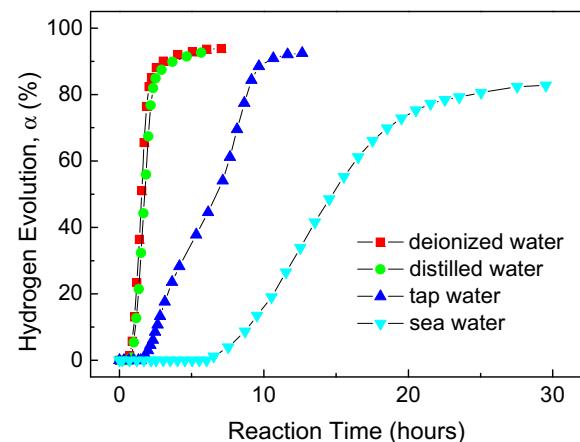


Fig. 2. H_2 evolution from different types of water using as-received Al powder at 40 °C without stirring.

Table 1

Reaction data of Al powder with four types of water at 40 °C.

Water types	Induction time (h)		MHGR ($\text{cm}^3 \text{H}_2(\text{min g-Al})^{-1}$) ^a	
	Stirring	Without stirring	Stirring	Without stirring
Deionized water	1.4	0.6	14.9	12.4
Distilled water	1.2	0.8	19.9	11.4
Tap water	13.5	2.0	4.6	2.7
Sea water	6.3	6.0	0.9	1.2

^a MHGR is obtained by the generated H_2 volume (normalized in the standard condition) divided by the time interval and the Al net weight.

material for portable application (the continuous hydrogen supply for a portable device could be realized by uninterruptedly adding the Al powder into water, because the new added Al powder would react with water and generate hydrogen successively).

Fig. 3 shows the Al–water reaction using four types of water at 40 °C with and without stirring. It is well known that stirring speeds up the chemical reaction, because in this case the contact between different reactants increases. However, the present results indicates that the Al–water reaction was retarded by the stirring, and the induction time for the reaction with stirring is longer than that without stirring (Table 1), especially for tap water, which is opposite to the behavior of ordinary chemical reaction. It is noticed that the reaction retarding behavior in sea water by stirring (Fig. 3(d)) is different from that in tap water, the increase in induction time in tap water by stirring is much longer than that in sea water.

As the pH value of four types of water has a small difference (6.5–7.6), in order to clarify the role of pH value in Al–water reaction dynamics, the water with different pH value was used to react with Al powder, as shown in Fig. 4, where the water with

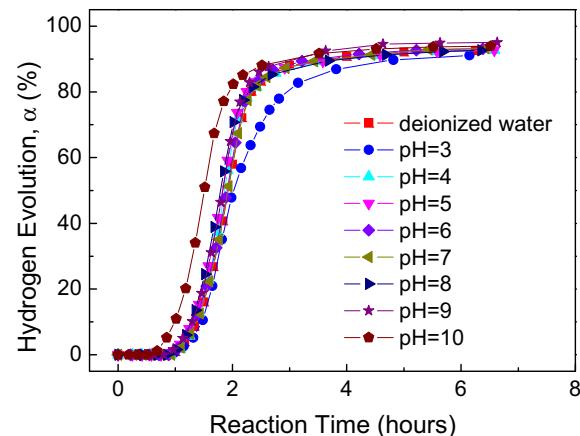


Fig. 4. H_2 evolution from water with different pH value using as-received Al powder at 40 °C without stirring, where the reaction result of Al with deionized water is added for comparison.

different pH value was obtained by adding a suitable amount of HCl or NaOH in deionized water. It can be seen that there is almost no impact on Al–water reaction dynamics when the pH value in water is between 3 and 9, indicating that the pH value in four types of water is not a factor responsible for their different reaction dynamics with Al.

Our trace species analysis experiment indicated that the detected concentration of trace metal cations and inorganic anions in deionized and distilled water is very few and negligible (<0.01 ppm). As the sea water has a high concentration of varieties of cations and anions, and firstly tap water was used to compare with deionized water. The concentration of different trace metal cations in tap water is shown in Table 2, where the other cations

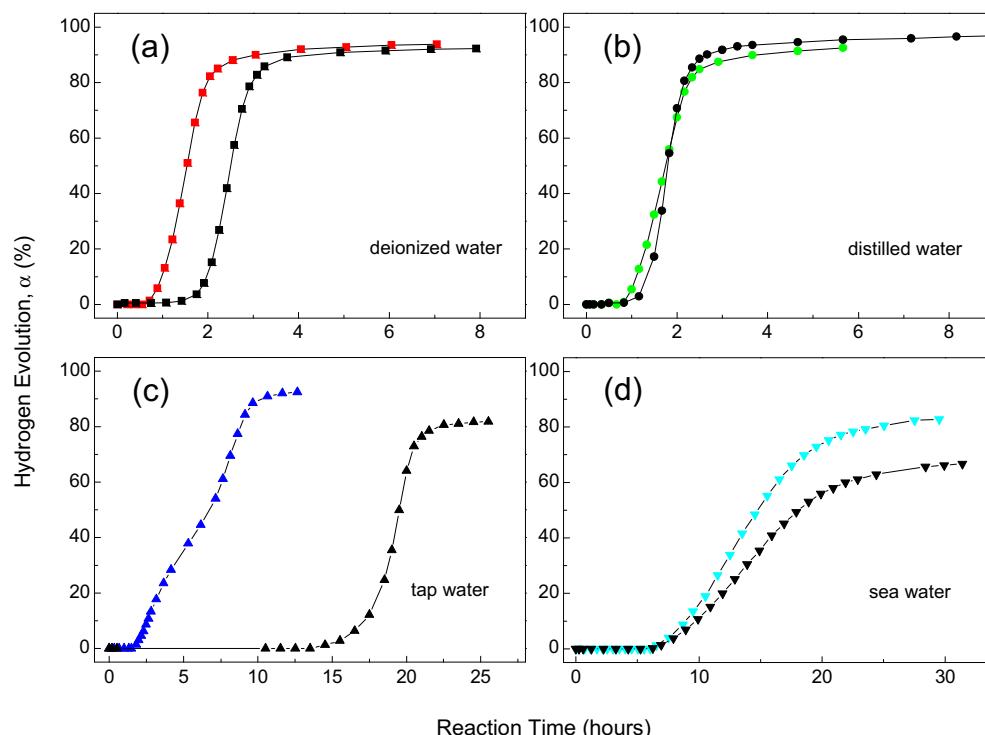


Fig. 3. H_2 evolution from different types of water using as-received Al powder at 40 °C with stirring (black dot curves) and without stirring (color dot curves). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

The concentration of trace cations in tap water.

Trace cations	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Zn ²⁺	Sr ²⁺
Concentration (ppm)	22.36	3.07	32.81	6.88	1.14	0.20

with a concentration of <0.01 ppm are not listed. It can be seen that the main trace cations in tap water are Na⁺, K⁺, Ca²⁺, Mg²⁺, Zn²⁺ and Sr²⁺. In order to clarify the effect of trace cations on the Al–water reaction dynamics, the hydrogen evolution from the water with each kind of trace cation or all kinds of trace cations in tap water using Al powder is shown in Fig. 5, where the trace concentration of each kind of cation in above water is the same as that in tap water. It can be seen that the trace metal cations in tap water is not the main factor responsible for the difference in Al–water reaction dynamics between tap and deionized water.

The concentration of different trace inorganic anions in tap and sea water is shown in Table 3, where the other inorganic anions with a concentration of <0.01 ppm are not listed. It can be seen that the main trace anions in tap and sea water are Cl⁻, SO₄²⁻, F⁻ and NO₃⁻ ions. In order to clarify the effect of trace anions on the Al–water reaction dynamics, the hydrogen evolution from the water with each kind of trace anion or all kinds of trace anions in tap water using Al powder is shown in Fig. 6, where the trace concentration of each kind of anion in above water is the same as that in tap water. It can be seen that the anions Cl⁻, SO₄²⁻ and NO₃⁻ have a negligible impact on the Al–water reaction dynamics, except for F⁻ ions. The F⁻ ions slightly retard the Al–water reaction and increase the reaction induction time up to ~1.1 h, however it can not account for the whole reaction dynamics of Al in tap water (the induction time ~2.0 h).

As the halide ions probably play a role in the Al–water reaction dynamics, the effect of Cl⁻ and F⁻ ions on the Al–water reaction is investigated. Fig. 7 shows the hydrogen evolution from water containing different amount of Cl⁻ ions using pure Al powder with stirring. It can be seen that Cl⁻ ions almost have no effect on the Al–water reaction dynamics, even if the concentration of NaCl is up to 3%. Fig. 8 shows the hydrogen evolution from water containing different amount of F⁻ ions using pure Al powder without and with stirring. It can be seen that F⁻ ions has a significant impact on the Al–water reaction dynamics, and the reaction induction time increases with increasing the F⁻ ion concentration. Furthermore,

Table 3

The concentration of trace inorganic anions in tap and sea water.

Water types	Cl ⁻ (ppm)	SO ₄ ²⁻ (ppm)	F ⁻ (ppm)	NO ₃ ⁻ (ppm)
Tap water	38.97	36.45	0.25	8.04
Sea water	10,603.00	1173.00	8.00	5.80

stirring greatly retards the Al–water reaction and increases the reaction induction time (Fig. 8(b)), which is similar to the results in Fig. 3, implying that trace F⁻ ions probably is a cause resulting in the reaction dynamics difference of Al with different water.

In addition to the inorganic salts dissolved in water, there is a trace amount of organic species in water. Table 4 gives the concentration of total organic carbon (TOC) in four types of water, which is a representation of total organic substances dissolved in water. It can be seen that the concentration of TOC in tap and sea water (~4.0 ppm) is higher than that in deionized and distilled water (~1.0 ppm). It is difficult to analyze the exact compositions of these organic substances, because their quantity is too little to be used in the practical composition analyses. As water comes from nature, the main trace organic species probably are the soluble organic acids, which originated from the decay and decomposition of botanies and animals in nature. For example, citric acid, tartaric acid and oxalic acid derived from root exudates are common organic substance in nature [31,32]. In order to clarify the effect of trace organic species on Al–water reaction dynamics, the above three typical organic acids were used to simulate organic substance in tap and sea water. Fig. 9 shows the hydrogen evolution from water containing different trace concentration of citric acid using Al powder with and without stirring. The citric acid has a significant impact on the Al–water reaction dynamics and the reaction induction time increases with increasing the citric acid concentration. Furthermore, stirring greatly retards the Al–water reaction and increases the reaction induction time (Fig. 9(b)), which is similar to the results in Fig. 3, implying that trace organic acids probably are another cause resulting in the reaction dynamics difference of Al with different water.

In order to quantitatively compare the reaction dynamics of tap water with that of trace organic acid solution, the hydrogen evolution from water containing a trace concentration of one organic acid using Al powder with and without stirring is shown in Fig. 10, where the trace TOC concentration in above water after adding one

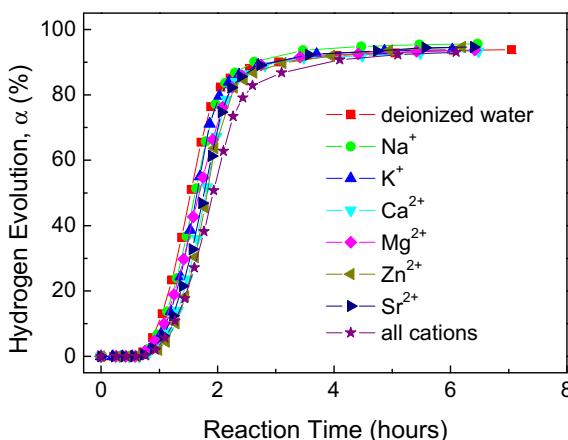


Fig. 5. H₂ evolution from water containing one or different kinds of cations using as-received Al powder at 40 °C without stirring, where the trace concentration of each kind of cation in above water is the same as that in tap water, and “all cations” represents the water contains all kinds of trace cations in tap water. The reaction result of Al with deionized water is added for comparison.

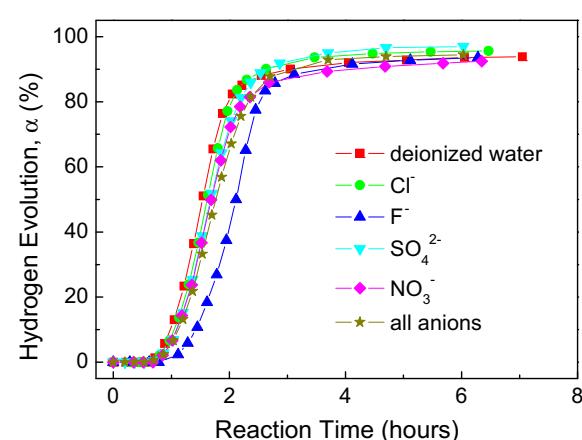


Fig. 6. H₂ evolution from water containing one or different kinds of anions using as-received Al powder at 40 °C without stirring, where the trace concentration of each kind of anion in above water is the same as that in tap water, and “all anions” represents the water contains all kinds of trace anions in tap water. The reaction result of Al with deionized water is added for comparison.

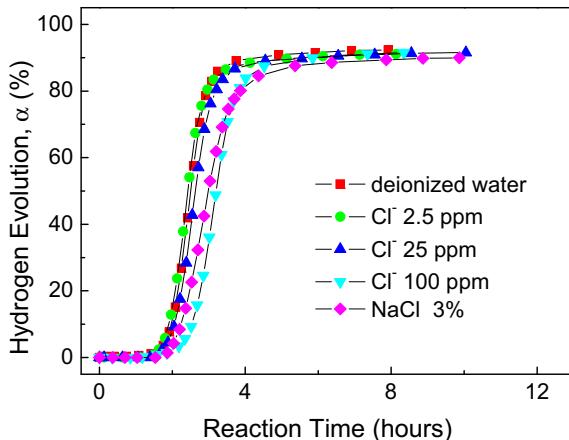


Fig. 7. H₂ evolution from water containing different amount of Cl⁻ ions using as-received Al powder at 40 °C with stirring. The reaction result of Al with deionized water is added for comparison.

organic acid is the same as that in tap water. It can be seen that citric acid, tartaric acid and oxalic acid have a similar effect on retarding the Al–water reaction, and in general speaking, the Al–water reaction dynamics after adding the above organic acids in deionized water with and without stirring is in good agreement with that in tap water.

3.2. Physicochemical mechanisms

It is well known that there is a dense passive oxide film on Al particle surface, which inhibits the corrosion of Al in water. When Al particles are put into water, a hydration process occurs in the passive oxide film [2,3], as shown in Fig. 11(a).



The hydration process involves the disruption of Al–O–Al bonds via hydrolysis to form Al–OH species, one Al–O–Al linkage is

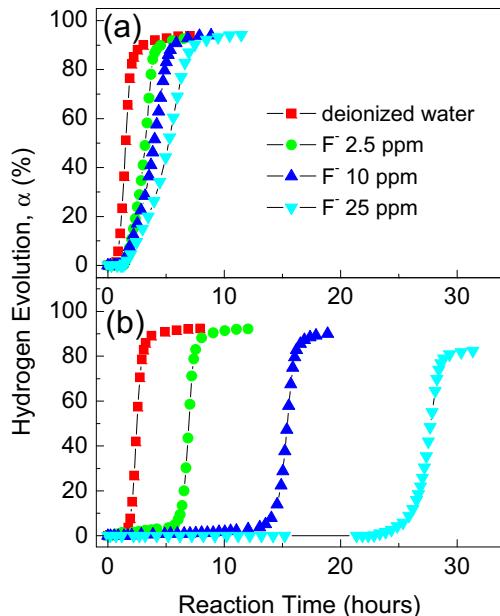


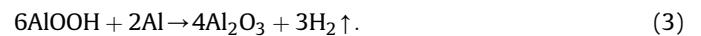
Fig. 8. H₂ evolution from water containing different amount of F⁻ ions using as-received Al powder at 40 °C (a) without stirring and (b) with stirring. The reaction result of Al with deionized water is added for comparison.

Table 4
The concentration of trace organic species in four types of water.

Water types	Deionized water	Tap water	Distilled water	Sea water
TOC ^a (ppm)	1.08	3.70	1.17	4.05

^a TOC is the concentration of total organic carbon in water.

broken to form two Al–OH for each water molecule consumed [2]. Upon hydration, aluminol groups ($\equiv\text{AlOH}$) forms on the oxide surface [33]. Extensive hydration reaction eventually produces oxyhydroxide or hydroxide phases such as AlOOH and Al(OH)₃ that are thermodynamically more stable than Al₂O₃ at mild temperature [3]. When the hydrated front meets the inner Al surface, condensation reactions can occur in which two hydroxide ions recombine to generate an oxide linkage and a water molecule (the reverse of hydrolysis), because aluminum hydroxide phases are known to be thermodynamically unstable in contact with metal Al,



In this case, the inner Al would react with water molecule and release hydrogen. Because of the limited H soluble capacity in Al particles and the low permeability of the hydrated oxide film toward H₂, H₂ molecules accumulate and form small H₂ bubbles at the Al:Al₂O₃ interface (Fig. 1 in Ref. [3]). When the pressure in H₂ bubbles exceeds a critical gas pressure that the hydrated oxide film can sustain, the film on the Al particle surfaces will be broken. Then the water directly contacts with inner Al and the reaction of Al with water continues. According to the above analyses, there is an induction time for the beginning of Al–water reaction, which is responsible for the hydration process in the passive oxide film, the H diffusion saturation in bulk Al and the accumulation of H₂ molecules in H₂ bubbles to reach the critical gas pressure. The existence of this induction time has been confirmed by this work.

When organic acids are present in water, organic acids can adsorb on the hydrated alumina surface by a surface complexation reaction [34–37], as shown in Fig. 11(b). Specific adsorption of organic acids at the aluminum oxide or hydroxide-solution

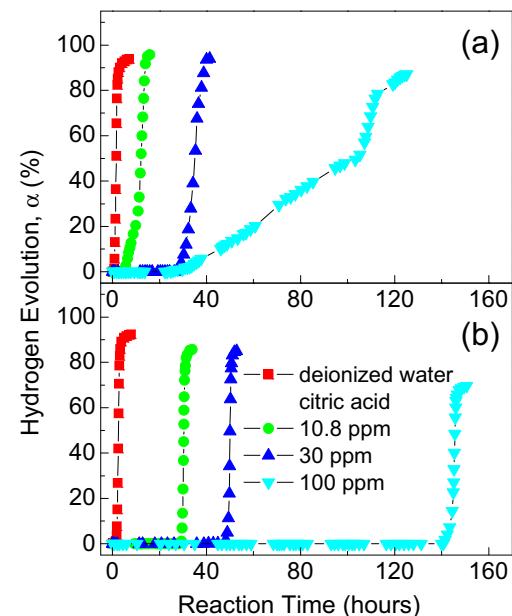


Fig. 9. H₂ evolution from water containing different trace concentration of citric acid using as-received Al powder at 40 °C (a) without stirring and (b) with stirring. The reaction result of Al with deionized water is added for comparison.

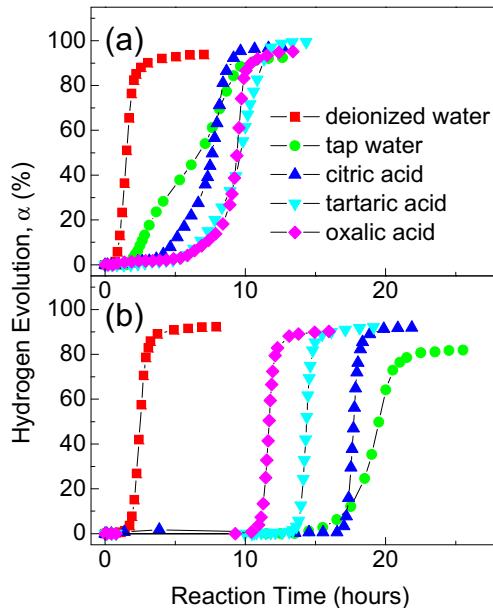
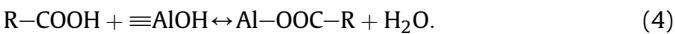


Fig. 10. H_2 evolution from water containing a trace concentration of different organic acid using as-received Al powder at 40 °C (a) without stirring and (b) with stirring, where the trace TOC concentration in above water after adding one organic acid is the same as that in tap water. The reaction result of Al with deionized water is added for comparison.

interface can be described as a surface coordination reaction using the ligand exchange model [36]. To a certain degree, the surface hydroxyl group can be understood as a Lewis base, which has an oxygen atom as a donor that can coordinate with protons or Al ions (Lewis acid). The underlying structural Al ions in the surface passive oxide film of Al particles are a Lewis acid, which can exchange the hydroxyl group for other coordinating anions [36]. Thus, the specific adsorption of a carboxyl acid at the alumina–water interface can be described as a ligand exchange, where the hydroxyl group is exchanged for a carboxyl group. According to the ligand exchange model, such an adsorption is a simple exchange of OH^- group for an R-COO⁻ group



After the surface complexation reaction, a stable Al-organic substance complex layer forms on the surface of passive oxide

film (Fig. 11(b)). For citric acid, tartaric acid and oxalic acid, their Al-organic substance complexes are very stable [35,37], which inhibit the H_2O transportation and retard the hydration reaction of the passive oxide film on Al particles so that the reaction induction time increases, as shown in Figs. 2, 9 and 10.

Similar to organic acids, F^- ions also have a complexing capacity. When F^- ions are present in water, stable Al-F complexes can form on the passive oxide film of Al particles [38–41],



which retard the hydration reaction of the passive oxide film on Al particles as well, leading to the increase in the reaction induction time, as shown in Figs. 6 and 8.

The above analyses explained why the Al–water reaction dynamics in tap and sea water is retarded relative to deionized and distilled water, because the tap and sea water has a higher concentration of TOC and F^- ions than the deionized and distilled water (Tables 3 and 4). In addition, stirring increases the contact between Al particles and organic acid or F^- ions, in this case more Al-organic substance complexes or Al-F complexes would cover on the Al particle surfaces at a shorter time than that without stirring. This is why stirring retards the Al–water reaction dynamics and greatly increases the Al–water reaction induction time, as shown in Figs. 3 and 8–10. The small reaction dynamics difference between deionized and distilled water with stirring shown in Fig. 3 probably results from the different types of trace organic species in them, because the purification procedure is different to get deionized and distilled water.

Usually the movement of anions is accompanied by cations due to the requirement of local charge balance, so the ion directional movement velocity driven by the concentration gradient probably is related to the total ion concentration in aqueous solution. Fig. 12 is a schematic representation of the ion directional movement in the aqueous solutions with a low and a high ion concentration. It can be seen that when the ion concentration in solution is low, the local charge balance makes an anion movement accompanied by a cation, and it likes an “anion–cation” binding body movement, similar to a binding electron moving in a semiconductor. When the ion concentration in the solution is high, the ion density in solution is high and the ions distribute everywhere, in this case the movement of anions in solution likes that on a uniform positive charge background, similar to a free electron moving in a conductor. It is clear that the moving velocity of anions in the solution with a low ion concentration is much slower than that with a high ion concentration.

As sea water has a much higher ion concentration than tap water, as listed in Table 3, this is also confirmed by the electrical conductivity of sea water (resistivity <50 Ω cm) and tap water (resistivity ≈ 4 k Ω cm). This means that the movement of organic acid and F^- ions in sea water is much faster than that in tap water. In this case, the time to cover Al particle surfaces by a saturation layer of Al-organic substance and Al-F complexes in sea water is much shorter than that in tap water, implying that the fast movement of organic acid and F^- ions in sea water makes the effect of stirring on Al–water reaction dynamics become small. This is why the reaction retarding behavior in sea water by stirring is different from that in tap water (Fig. 3).

To further validate the reaction mechanism proposed in Fig. 11, the water after the reaction with Al was reused as the reactant (R-filtrate), which was obtained by filtering the reaction solution of Al with water using the filter paper. Figs. 13–15 show hydrogen evolution from the R-filtrates using Al powder at 40 °C. It can be seen that the difference in Al–water reaction dynamics using deionized water and its R-filtrate is small,

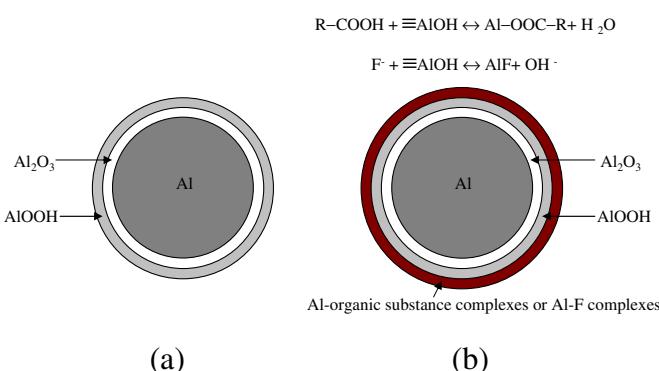


Fig. 11. Schematic representation of the surface structure of an Al particle in water (a) without and (b) with organic acids or fluorides, where the organic acids and F^- ions would form complexes with aluminol groups on Al particle surface to impede the hydration process of Al surface oxide film.

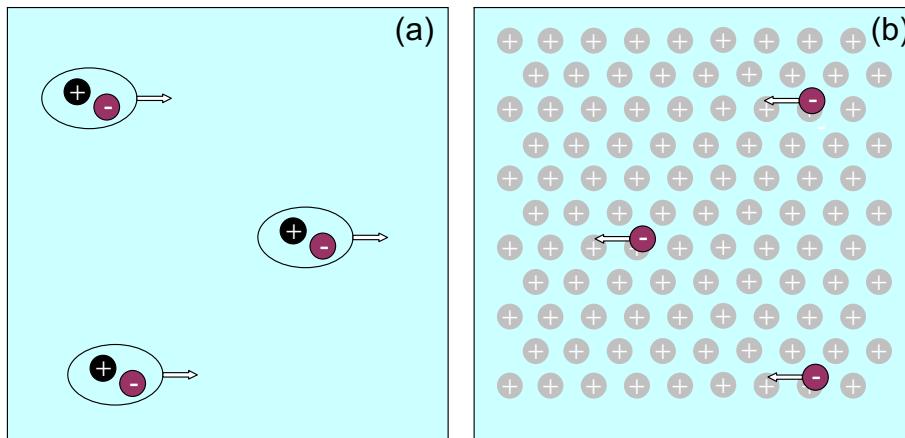


Fig. 12. Schematic representation of the organic acid or F^- ion movement in aqueous solutions with (a) a low ionic concentration and (b) a high ionic concentration, where the ion movement in (a) likes the binding electrons moving in a semiconductor, and that in (b) likes the free-electrons moving in a conductor.

implying that there are few trace species in deionized water that affect the Al–water reaction (Fig. 13(a)). For tap water, its R-filtrate almost has the same Al–water reaction dynamics as deionized water, indicating that the trace organic acids and F^- ions were taken away with the reaction byproduct due to the Al–organic substance and Al–F complexes absorbing on the passive oxide films (Fig. 13(b)). Meanwhile, as-received tap water was directly filtered using the filter paper (U-filtrate) and used to react with Al powder. However, the Al–water reaction using tap water is almost the same as that using its U-filtrate, implying that the trace organic acids and fluoride are dissolved in water. The R-filtrates come from the Al–water reaction using the water with a trace concentration of F^- ions or oxalic acid have a similar behavior as that of tap water (Fig. 14), further confirmed the proposed mechanisms in Fig. 11.

As sea water has a higher trace F^- ion concentration than tap water, its reaction retarding behavior should result from the synergic effect of F^- ions and organic acids. Its R-filtrate behaves a different reaction dynamics, compared to those from tap water and the water with a trace concentration of F^- ions or oxalic acids, as shown in Fig. 15. The R-filtrate come from sea water still has a retarding effect on Al–water reaction even the number of times of the Al reaction with sea water and then filtering is up to three, implying that its R-filtrate still has a trace amount of F^- ions and oxalic acids.

Fig. 16 shows the X-ray diffraction patterns of pure Al powder and those after reaction in deionized water, tap water and 100 ppm citric acid solution. It can be seen that the reaction byproduct depends on the water quality. The byproducts of Al–water reaction in deionized water are bayerite and boehmite, while those in tap water and citric acid solution are only boehmite.

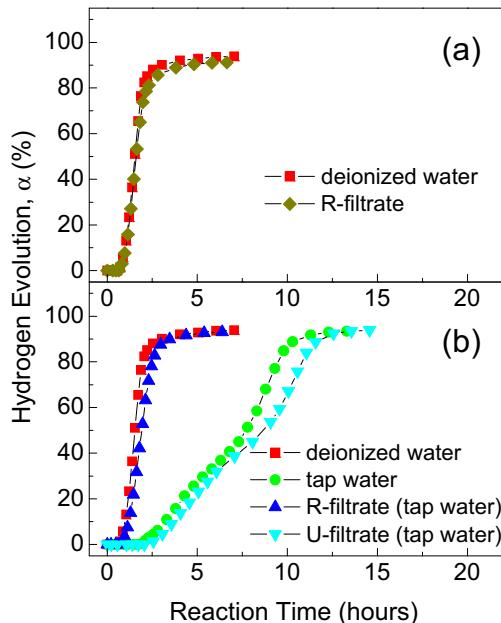


Fig. 13. H_2 evolution from (a) deionized water and (b) tap water using as-received Al powder at 40 °C without stirring, where U-filtrate is the water obtained by filtering as-received water using a filter paper, and R-filtrate is the water obtained by filtering the reaction solution of Al with water using the filter paper.

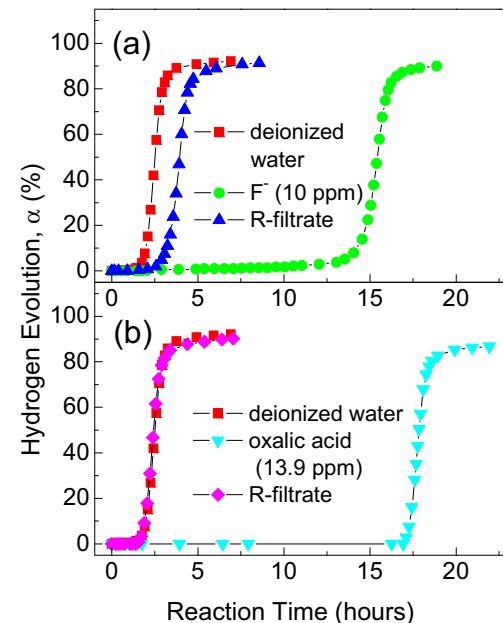


Fig. 14. H_2 evolution from the water with a trace concentration of (a) F^- ions and (b) oxalic acid, respectively, using as-received Al powder at 40 °C with stirring, where R-filtrate is the water obtained by filtering the reaction solution of Al with water using a filter paper. The reaction result of Al with deionized water is added for comparison.

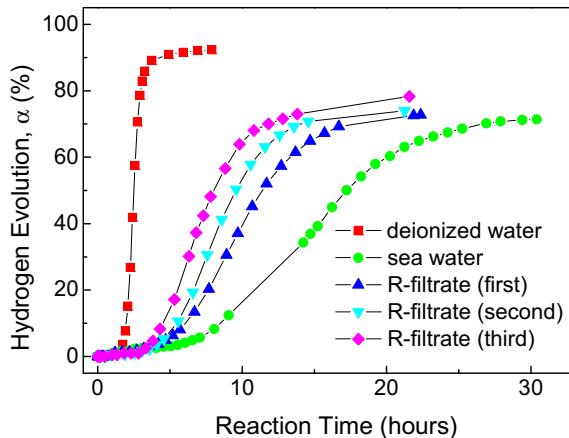


Fig. 15. H_2 evolution from sea water using as-received Al powder at 40 °C with stirring, where R-filtrate is the water obtained by filtering the reaction solution of Al with sea water using a filter paper, and the sequence number in the parenthesis represents the number of times of the Al reaction with sea water and then filtering. The reaction result of Al with deionized water is added for comparison.



The above results proved that an Al–organic substance and Al–F complex layer on Al particle surfaces inhibits the transportation of water molecules in the passive oxide film so that their reaction byproduct is a hydromorphic hydroxide, i.e. boehmite.

The F^- ions and organic acids in water retard the Al–water reaction, which is unfavorable for enhancing the hydrogen generation rate. However, this effect probably can be used to prevent Al powder oxidation in a humid environment or to inhibit the Al–water reaction in anode of Al–air battery. Fig. 17 shows that a 10.8 ppm citric acid increased the Al–water reaction induction time

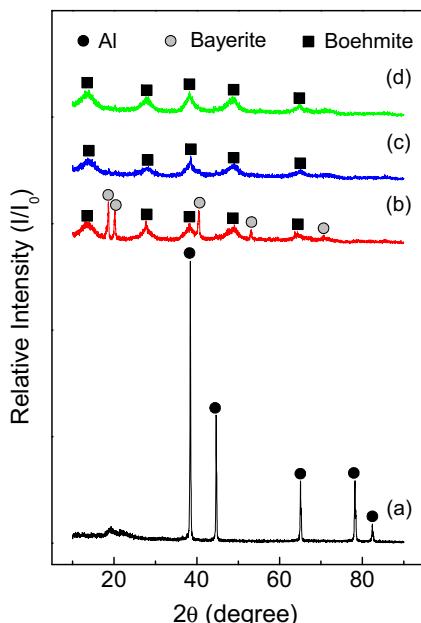


Fig. 16. X-ray patterns of (a) as-received Al powder, and that after reaction in (b) deionized water for 7.1 h, (c) tap water for 12.7 h and (d) the citric acid solution with a trace concentration of 100 ppm for 125.2 h, respectively, at 40 °C without stirring.

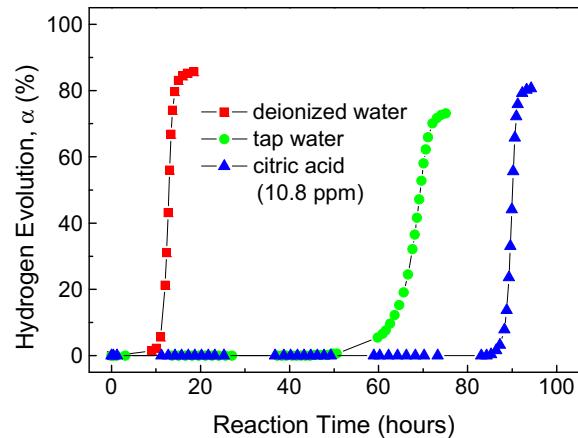


Fig. 17. H_2 evolution from different aqueous solutions using as-received Al powder at 30 °C with stirring, where the trace concentration of citric acid in water is 10.8 ppm.

from ~10 h up to ~85 h at a temperature of 30 °C, showing a potential in this kind of application.

4. Conclusions

In this work, the effect of trace species in water on Al–water reaction at a mild temperature was investigated. The results indicated that the trace organic acids and F^- ions have a significant impact on Al–water reaction dynamics, while the effect of other cations and anions in water is negligible. The organic acids and F^- ions form complexes with aluminol groups on Al particle surfaces and impede the hydration process of Al surface oxide film, leading to an increase in the induction time for the beginning of Al–water reaction. A mechanism was proposed to explain the different Al–water reaction dynamics behavior in tap and sea water, based on the ion concentration and local charge balance. The present research indicates that water quality is important for the Al–water reaction to generate hydrogen. Meanwhile, this effect probably can be used to prevent Al oxidation in a humid environment or other undesirable Al–water reaction.

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